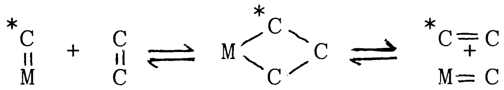
CHEMISTRY LETTERS, pp. 623-626, 1980. © The Chemical Society of Japan 1980

ON THE REVERSIBILITY OF METAL CARBENE FORMATION PROCESS IN OLEFIN METATHESIS REACTION OVER $MoO_x/\beta\text{-}TiO_2$ CATALYST

Katsumi TANAKA, Koshiro MIYAHARA, and *Ken-ichi TANAKA
Research Institute for Catalysis, Hokkaido University, Sapporo 060
*Faculty of Engineering, Hokkaido University, Sapporo 060

Co-isomerization of d_0- and d_8-*cis*-2-butene was carried out on a novel catalyst, $MoO_x/\beta\text{-}TiO_2$ $(2.9>x>2.3)$, which is active for olefin metathesis reaction without inter- and intra-molecular hydrogen scrambling of olefins. The ratio, $d_4/(d_0+d_8)$, in produced *trans*-2-butene was found to be zero at the initial stage of the reaction, indicating a type of *cis-trans* isomerization by intra-molecular metathesis.

Metal carbene and metallocyclobutane intermediates have been generally accepted for catalytic olefin metathesis reactions.[1)] However, detailed behavior of metal carbene intermediates is still unsolved. In order to throw light on this problem, metathesis reactions of deuterium-labelled olefins were performed on a novel catalyst, $MoO_x/\beta\text{-}TiO_2$, on which metathesis reaction took place with neither inter-molecular hydrogen scrambling nor isomerization via alkyl or carbonium ion intermediates.[2)]



To confirm the absence of intra-molecular hydrogen transfer in olefin molecule during its metathesis reaction, 1,1,2-d_3-propene (94.1%) was admitted to $MoO_x/\beta\text{-}TiO_2$ catalyst. If the intra-molecular hydrogen transfer to give 2,3,3-d_3-propene would take place, metathesis reaction of these propenes might produce 2-d_1- and 1,1,2,3,3-d_5-propene by degenerate metathesis and 1,1-d_2- and d_0-ethylene as well as 1,1,2,3-d_4- and 1,1,2,3,4,4-d_6-2-butene by productive metathesis. The result was not the case as shown in Table 1, which proves that the metathesis reaction proceeds on this catalyst with neither inter-molecular nor intra-molecular hydrogen exchange reaction. The amount of total 2-butene less than that of ethylene in Table 1 gives evidence for the preferential adsorption of 2-butene.

In case of the reaction of a 1:1 mixture of d_0- and d_8-*cis*-2-butene on $MoO_x/\beta\text{-}TiO_2$, *trans*-2-butene consisting of d_0-, d_4- and d_8-isomers was formed without any induction,[2,3)] showing again the *cis-trans* isomerization was exclusively caused by the degenerate metathesis reaction of 2-butene. Taking account of metallocyclobutane intermediate generally accepted for metathesis reaction, four cases as shown in Scheme can be considered for the formation of *trans*-2-butene.

Table 1 Composition and deuterium distributions of propene, ethylene, *cis*- and *trans*-2-butene produced in the metathesis reaction of 1,1,2-d_3-propene (10.0mmHg) on 6.7wt% $MoO_x/\beta\text{-}TiO_2$ (1.0g) at room temperature.

		Deuterium distributions (%)						
Product	Comp.(%)	d_0	d_1	d_2	d_3	d_4	d_5	$d_{6\sim}$
Propene	87.4	0	2.1	4.2	92.2	0	1.6	0
Ethylene	11.3	0	0	4.1	6.1	89.8	–	–
t-2-Butene	1.2	0.5	2.4	91.0	0.6	4.7	0.8	0
c-2-Butene	0.2	2.4	2.8	90.4	1.1	3.3	0	0

Table 2 Relative amounts of deuterio-isomers of *trans*-2-butene expected through metallocyclobutane intermediates formed from respective metal carbenes and *cis*-2-butenes.

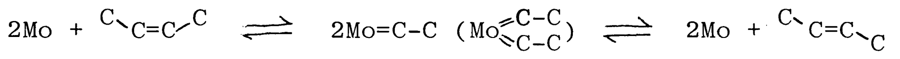
Combi. / Case	$\mathrm{M{=}C{-}C}$ + $\mathrm{C{\backslash}C{=}C{/}C}$	$\mathrm{M{=}C{-}C}$ + $\overset{*}{\mathrm{C}}{\backslash}\overset{*}{\mathrm{C}}{=}\overset{*}{\mathrm{C}}{/}\overset{*}{\mathrm{C}}$	$\mathrm{M{=}}\overset{*}{\mathrm{C}}{-}\overset{*}{\mathrm{C}}$ + $\mathrm{C{\backslash}C{=}C{/}C}$	$\mathrm{M{=}}\overset{*}{\mathrm{C}}{-}\overset{*}{\mathrm{C}}$ + $\overset{*}{\mathrm{C}}{\backslash}\overset{*}{\mathrm{C}}{=}\overset{*}{\mathrm{C}}{/}\overset{*}{\mathrm{C}}$	d_4/d_0+d_8 of trans-2-Butene
I	$3d_0$	$2d_4+d_8$	d_0+2d_4	$3d_8$	0.5 (4/8)
II-1	$2d_0$	d_4+d_8	d_0+d_4	$2d_8$	0.3_3 (2/6)
II-2	d_0	d_4	d_4	d_8	1.0 (2/2)
II-3	d_0	d_8	d_0	d_8	0.0 (0/4)

$=C{-}C$ --- $=CH{-}CH_3$, $=\overset{*}{C}{-}\overset{*}{C}$ ---- $=CD{-}CD_3$

Since $Mo{=}CHCH_3$ and $Mo{=}CDCD_3$ are produced from d_0- and d_8-*cis*-2-butene, four types of combination of metal carbene with *cis*-2-butene to form metallocyclobutane intermediates are possible as listed in Table 2. For each type of combination, four cases, as shown in Figure 1, are possible for fission of metallocyclobutane into *trans*-2-butene and metal carbene and the ratio, $d_4/(d_0+d_8)$, of *trans*-2-butene will take steady values of 0.5, 0.3_3, 1.0 and zero for the cases I, II-1, II-2 and II-3, respectively, as equivalent $Mo{=}CHCH_3$ and $Mo{=}CDCD_3$ are formed from equivalent d_0- and d_8-*cis*-2-butene.

The observed value of the ratio, $d_4/(d_0+d_8)$, of produced *trans*-2-butene agrees with none of the cases. This ratio is likely to be extraporated to zero at the initial stage of reaction, and rapidly increased to the equilibrium value, 1.0, as the reaction proceeded. This result indicates preferential formation of d_0- and d_8-*trans*-2-butene from d_0- and d_8-*cis*-2-butene, respectively, that is, the preferential intramolecular metathesis at the initial stage of reaction. Furthermore, the time course of the ratio, $d_4/(d_0+d_8)$, of *trans*-2-butene from zero to 1.0 can not be interpreted by the effects of these cases. It is inconceivable that, instead of case II-1, case II-3 occurs selectively at the initial stage and then shifts to case II-2 with progress of the reaction.

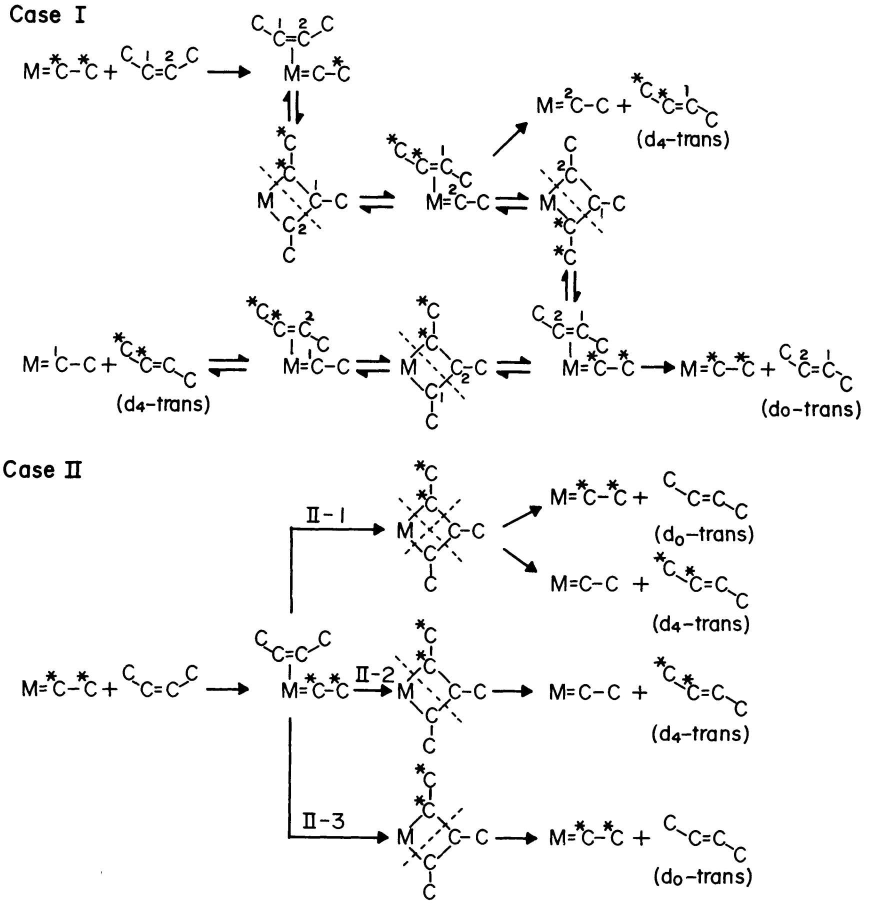
Taking into account that the *cis-trans* isomerization on $MoO_x/\beta\text{-}TiO_2$ was caused exclusively by metathesis, the *cis-trans* isomerization of 2-butene at its initial stage is probably atributed to the recombination of metal carbenes as



$$2\mathrm{Mo} + {}^{\mathrm{C}}\diagdown\mathrm{C}=\mathrm{C}\diagup{}^{\mathrm{C}} \rightleftharpoons 2\mathrm{Mo}=\mathrm{C}-\mathrm{C}\ \left(\mathrm{Mo}\begin{smallmatrix}\mathrm{C}-\mathrm{C}\\ \mathrm{C}-\mathrm{C}\end{smallmatrix}\right) \rightleftharpoons 2\mathrm{Mo} + {}^{\mathrm{C}}\diagdown\mathrm{C}=\mathrm{C}\diagdown{}_{\mathrm{C}}$$

MO: Mo ion.

Scheme



Scheme

Case I ; Rapid equilibration between C_2 alkylidene and adsorbed 2-butene *via* metallocyclobutane precedes the desorption of *trans*-2-butene.

Case II; The reaction between metal carbene - olefin complex and metallocyclobutane is irreversible.

II-1; Two types of fission of metallocyclobutane into metal carbene and olefin are brought about in equal probability.

II-2; C_2 alkylidene of metal carbene is necessarily introduced into *trans*-2-butene.

II-3; None of C_2 alkylidene of metal carbene is introduced into *trans*-2-butene.

* We neglect in these cases any isotope effect as well as stereo-selectivity attributed to the stability of metallocyclobutane intermediates.[4)]

The time course of the ratio, $d_4/(d_0+d_8)$, of *trans*-2-butene might be caused by the increase of metallocyclobutane, which accelerates the formation of d_4- as well as d_0- and d_8-*trans*-2-butene through the chain reaction such as cases I and II-1 shown in the Scheme.

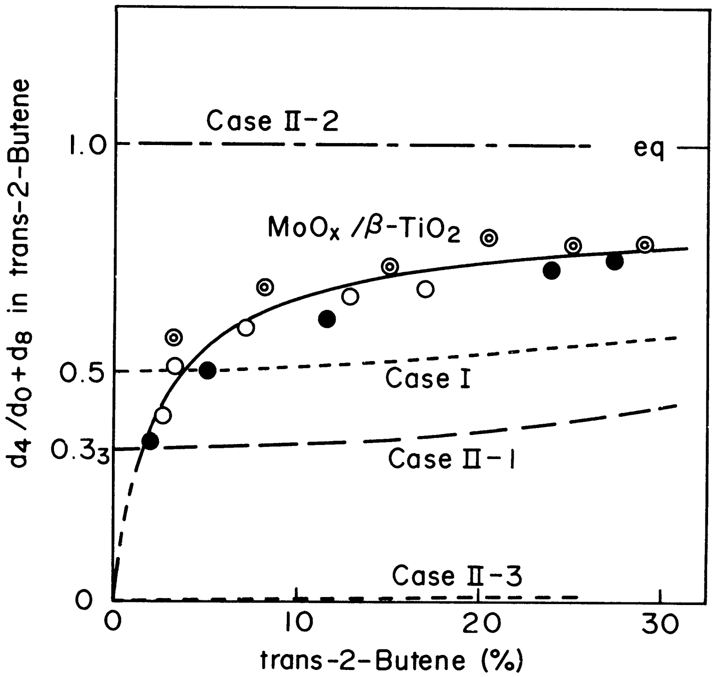


Figure 1 Time course of the ratio, $d_4/(d_0+d_8)$, of *trans*-2-butene produced in the metathesis reaction of a 1:1 mixture of d_0- and d_8-*cis*-2-butene.

6.7 wt% $MoO_x/\beta\text{-}TiO_2$ 0.3g

Pressure (mmHg)	Reaction Temperature (°C)
56.2	23
16.0	- 8
32.5	-10

REFERENCES

1). for instance, J. J. Rooney and A. Stewart, "Catalysis (Specialist Periodical Reports)" vol. 1 (ed. C. Kemball) chap 8, J. Chem. Soc., (1977).

2). Katsumi Tanaka, Ken-ichi Tanaka and K. Miyahara, J. Chem. Soc. Chem. Comm., 314 (1979).

3). Katsumi Tanaka, Ken-ichi Tanaka and K. Miyahara, Shokubai (Catalyst), 21, 73P (1979).

4). W. B. Hughes, J. Chem. Soc. Chem. Comm., 431 (1969).

J. L. Bilhou, J. M. Basset, R. Mutin and W. F. Graydon, J. Amer. Chem. Soc., 99, 4083 (1977).

C. P. Casey and H. E. Tuinstra, ibid., 100, 2270 (1978).

M. Leconte and J. M. Basset, ibid., 101, 7296 (1979).

(Received March 12, 1980)